Investigation of product coking induced by hot recycle solids
in the KENTORT II fluidized bed retort.

D.N. Taulbee and S.D. Carter
University of Kentucky-Center for Applied Energy Research
Lexington, KY 40511

Keywords: coke, shale oil coke, fluidized bed.

ABSTRACT. The mechanism and extent to which oil shale pyrolysis products undergo secondary coking reactions is governed to a large degree by the nature and temperature of the surfaces with which these products interact. Since the composition and temperature of the solids utilized to transfer heat in the KENTORT II fluidized-bed reactor can, to some extent, be controlled, it is important to determine the relative coke forming activity of these solids at process temperature in order to maximize product yield. With this objective, an apparatus has been constructed that permits shale oil vapors generated in one fluidized bed to pass over selected substrates in a second fluidized bed. The reactivity of the solid as a function of exposure time is monitored with an on-line mass spectrometer while total carbon deposition is determined post-run by ultimate analysis of the substrate. Over the temperature range of 530-660^0 C, the order of substrate reactivity was determined to be kaolinite > combusted shale > illite > gasified shale > pyrolyzed shale > sand. Surface area/pore volume data for the various substrates will be presented and discussed in terms of coking activity.

INTRODUCTION. One of the factors that ultimately controls oil yield during oil shale pyrolysis is the extent of secondary reactions, i.e, cracking and coking, that occur within the reactor[1]. These reactions in turn, are governed by several factors including reactor temperature, product residence time, resource properties, and the types of solid surfaces which the vapor phase hydrocarbons contact at elevated temperature. For a given resource, short of resorting to high H_2 partial pressures, the simplest means of enhancing liquid yield is to reduce the product residence time. For this reason, among others, fluidized bed retorting is regarded as an attractive technology for processing the eastern US oil shales, and consequently, has been under continuing development at the UK-CAER since about 1982[2] in a process termed KENTORT II.

Since one of the more effective means to transfer heat in a fluidized bed reactor is through direct addition of heat carrying solids, solids recycle is thought to be the most practical approach for a large scale operation. Accordingly, a KENTORT II prototype operated at the CAER was designed to simulate commercial operation by recycling hot solids to the pyrolyzer from both a fluidized bed gasifier and combustor. However, delivery of hot solids to the pyrolyzer promotes secondary cracking and coking reactions resulting in lower oil yield. Therefore, since the temperature, concentration, and composition of the heat transfer solids can, to some extent, be controlled in the KENTORT design, it is vital that the reactivity of the heat-carrying solids be characterized at process temperature in order to minimize these detrimental reactions.

Several, often ingenious, strategies have been used to investigate the cracking and coking of shale oil over a solids substrate bed. However, all these techniques have suffered from an inability to closely simulate the solids/HC product interactions that take place in a continuous, solids recycle operation. For example, Levy et al.[3] continuously injected Fischer assay shale oil into a reactor where the shale oil was vaporized then passed through a bed of solids. Though informative, the HC stream does not have the same composition or tendency toward coke formation as freshly generated

shale oil vapors, particularly for shale oils that contain significant amounts of non-volatile components. In an investigation reported by Coburn et al.,[4] a pulse of oil shale was dropped into a fluidized bed pyrolyzer with the resulting vapors passed through a packed bed of solids. While this technique lends itself well to kinetic measurements, it suffers from the fact that the pyrolysis products differ in nature and concentration (and therefore reactivity) as a function of time. Rubel et al.[5] connected a packed bed pyrolyzer in series with a packed bed of solids in the same furnace then subjected both beds to the same heating profile. While this technique provides information on the relative substrate reactivity, its transient nature is unsuitable for kinetic measurements, nor does it simulate fluidized bed conditions.

To realistically examine both the kinetics and reaction mechanisms, an apparatus has been constructed which permits shale oil vapors generated in one fluidized bed to pass over selected substrates in a second bed. Since the oil product is at no time cooled or removed from the reactor and the time for non-catalyzed secondary reaction to occur is minimal, product loss reactions are thought to closely simulate those that occur within a circulating solids fluid bed reactor. Substrates can be fed in either a batch or continuous mode. In the batch mode, a given substrate is heated to reaction temperature then exposed to shale oil vapors for a selected time period. Carbon deposition onto the solid is monitored in real-time using an on-line mass spectrometer and total deposition verified by elemental analysis of the substrate following exposure.

Because the KENTORT concept utilizes a combination of gasified and combusted shale particles as the heat transfer medium, examination of these materials is emphasized.

EXPERIMENTAL. The oil shale used in this study was the CLE003 master sample from Fleming County, Ky.[6] The solid substrates examined and reactor conditions used are given in Tables 1 and 2. In addition to examining all of the substrates without pretreatment, aliquots of the gasified and combusted shale were placed in a solution of either 0.005 N NaOH or HCl overnight, thoroughly rinsed with deionized H_2O, then dried prior to testing.

The coking apparatus and procedures used are described in detail elsewhere.[7] Following is a condensed description.

Apparatus. The apparatus consists of two vertically aligned fluidized beds (7.6 cm i.d.) that share a common fluidizing medium and are heated externally by two dual-zone electrical furnaces (Figure 1). The fluidizing gas, N_2 in this study, is preheated then routed to the lower fluidized bed maintained at 530° C for all runs. Raw oil shale is metered by a N_2-purged screwfeeder into the lower fluidized bed where the level of solids is maintained at 7.6 cm by an exit standpipe.

In the upper portion of the apparatus, a vertical baffle divides the pipe into two unequal sections (73% and 27% of the cross sectional area). The larger section contains a fluidized bed of solids, and the smaller section provides a bypass-path for the fluidizing stream. A semi-butterfly valve beneath the baffled section selects the upward path for the pyrolysis product stream and is coupled to a three-way valve that routes a balancing gas to injection ports on either side of the baffle such that gas flows through both chambers regardless of the butterfly valve position. The balancing gas flow serves to maintain a constant total N_2 flow from the reactor, fluidize the upper bed, provide a gas seal for the semi-butterfly valve, and is some experiments, is used as a pretreatment gas for the substrate. A purge gas, argon, is introduced into the seal assembly of the semi-butterfly valve to inhibit coke formation and serve as a tracer gas to facilitate mass spectrometer analyses by correcting for pressure surges, changing flowrates, and instrumental fluctuations.

The balancing gas and the pyrolysis/fluidization stream are joined in the uppermost portion of the reactor. A split of this stream is drawn through a heated combustion tube (600° C) filled with a Pt/Al_2O_3 catalyst to expedite combustion. Downstream from the combustion tube, a heated

(280°C), 0.3 mm fused silica capillary continually samples the combustion gases and routes them directly to the inlet of a VG model EGA 300MM quadrupole mass spectrometer (QMS) operating in the multiple ion monitoring (MIM) mode. The masses selected for continuous monitoring include 40 (Ar); 12 (C-to confirm mass 44); 18 (H_2O); 28 (N_2); 32 (excess O_2 from combustion); 44 (CO_2); 46 (NO_2); 64 (SO_2); and 42 (C_3H_6-to verify combustor performance). All selected masses were sampled at approximately 1.5 second intervals. Total product transit time from the reactor to the QMS detector was roughly 1 second.

Procedure. Following system heat-up, raw shale feed is initiated with the semi-butterfly valve positioned so that pyrolysis products bypass the upper, substrate bed (i.e."bypass" position). At this point, the QMS is used to verify combustor operation and check overall system performance.

Next, ~100 g of substrate is loaded to the upper bed which is fluidized by the balancing N_2 gas. When the substrate reaches reaction temperature, QMS data collection is initiated and a baseline established. After approximately 3 minutes (>100 QMS scans), the semi-butterfly valve is rotated so that the upper bed is now fluidized by the pyrolysis stream from the lower bed and maintained in the 'fluidize' position for a selected time interval (5-15 minutes is typical). The valve is then returned to the bypass position and the substrate solids are immediately drained from the bed into a purged collection flask. QMS data collection is continued for at least 3 minutes to re-establish the baseline. The solids receiver flask is removed and replaced with an empty one and the procedure repeated.

Following exposure and recovery, each batch of substrate is weighed and ultimate analyses are performed using standard methods. Surface area and pore volume measurements by N_2 adsorption and Hg porosimetry are conducted on selected substrates. Total surface area data shown in this report represent the sum of meso and macro surface area from Hg porsimetry and BET micro surface area from N_2 adsorption. Pore volume data are from Hg porsimetry.

Part of the post-run data manipulation involves taking the ratio of the combustion gas the tracer gas intensity. By doing so, changes in selected elemental concentrations, particularly carbon, could be observed with minimal interference from changing measurement conditions that frequently occur during a run. These uncontrolled measurement variations include pressure fluctuations, changing combustor or capillary transfer tube flowrates, QMS drift, etc., and result in variations in the absolute level of combustion gases reported by the QMS that are not related to coking loss.

Results and Discussion. The method as described in this manuscript detects only those coking losses resulting from interaction between HC pyrolysis products and the solid substrate to which they are exposed. The apparatus was not configured to probe cracking reactions which will be examined in future experiments involving continuous substrate feed and model compound investigations. Nevertheless, because coking losses account for a significant reduction in oil yield in solid recycle systems and carbon deposition can affect the solids reactivity, the study of coking kinetics is crucial to yield optimization.

Two independent measures of carbon deposition were obtained. The first was calculated from ultimate analysis of the substrate prior to and following HC exposure. The main disadvantage with this approach is that numerous runs are required to establish the deactivation rate for a particular solid under a given set of conditions. Further, at low carbon concentrations, the analytical scatter of the ultimate analysis becomes significant and trace O_2 in the fluidizing gas is a potential problem. Therefore, a complementary measure of carbon deposition is required to provide an on-line determination of coke formation that is less prone to error at low conversion.

In the system described, the rate of carbon deposition onto a solid substrate can be inferred by measuring the total vapor phase carbon that exits the reactor in the by-pass mode (pyrolysis stream by-passes substrate bed) and comparing to the carbon that exits in the coking mode (pyrolysis stream

passes through substrate bed). However, accurately measuring total vapor phase carbon in a pyrolysis stream is not trivial. Collecting the product oil with the required precision is impractical in a fluid bed process due to numerous parameters that affect collection efficiency, i.e, HC concentration, fluidizing velocity, compositional changes due to cracking, etc. Attempts to measure the total HC product with a flame ionization detector (FID) have been reported.[8,9,10] However, FID measurement suffers from a variety of quantitative flaws including a small, nonlinear response to HC's of differing size or type, insensitivity to heteroatoms, and problems with aerosol formation and condensation of larger components prior to measurement. In comparison, the combustion/QMS approach utilized in this work, rapidly combusts the product stream before condensation or aerosol formation can occur and avoids non-linearity problems by monitoring a single species (CO_2) over a reasonably narrow concentration range. In addition, total N and S deposition can potentially be measured as NO_2 and SO_2 though problems with apparent reaction between H_2S and substrate iron have been encountered.

A typical coking sequence is illustrated by the QMS CO_2/Ar ratio in Figure 2b. With the *semi-butterfly* valve in the initial bypass position, the CO_2/Ar ratio is near constant. Upon switching the valve to 'fluidize', the ratio immediately drops to a minimum then makes an asymptotic approach to a new constant ratio. The initial plunge in the CO_2/Ar ratio is apparently due to rapid transport of oil vapor into the substrate pores. The ratio rises as the concentration within the pores nears the extraparticle concentration. When the valve is returned to bypass, the original baseline is restored.

There is a good deal of scatter apparent in the CO_2/Ar ratio of Figure 2b (likewise for NO_2 and SO_2). However, the measured fluctuations are real and due to rapid changes in the CO_2 concentration since the absolute intensity of Ar tracer, fluidizing N_2, and excess combustion O_2 remain relatively constant. This rapid change in CO_2 intensity is assigned to a number of sources including fluctuations in the shale feed rate over short time intervals, the chaotic nature of a bubbling fluid bed reactor, fines carryover to the combustor, and perhaps particle-to-particle kerogen content variations. The first two are believed to account for the bulk of the observed scatter.

Although the QMS baseline scatter is pronounced, conversion of shale oil vapor to coke was higher than the scatter under all study conditions. However, due to the data scatter, instead of directly integrating the raw data, a least-squares curve was first fitted to the data and the area between the fitted curve and a least-squares line fitted to the baseline data was determined. The 2-parameter functional form (excluding the intercept) that best fit the response curves for all runs was a decaying exponential form (Eq.1).

$$C_{solid} = a + b(1 - \exp(-ct)) \qquad (1)$$

The area between the region described by this curve and the CO_2/Ar baseline was then integrated and related to the increase in carbon content of the substrate through a proportionality constant. This constant was calculated by taking the ratio of the rate of volatile carbon production from the pyrolysis zone (determined by elemental analysis of the pyrolyzed shale) to the baseline CO_2/Ar ratio.

The coke formation data from integration of Equation 1 was then averaged with the substrate ultimate analysis. These average values are shown plotted in Figures 3 as a function of exposure time and substrate bed temperature. With the possible exception of sand, all substrates showed a higher coking rate with temperature. However, this change was small enough to suggest that coke formation was, for the most part, mass transfer limited.

Also shown in Figure 3, are coke deposition data for combusted and gasified shales that were pretreated in either NaOH or HCl (0.005 N). In all cases, coking onto the treated substrates was not significantly different than coking onto the untreated substrate. This suggests that the rate of coke

formation on the combusted or gasified shale substrates was not dominated by ionic surface sites.

The plots of Figure 3 indicate the relative coking activity to follow the order of Sand < pyrolysed < gasified < illite < combusted < course kaolinite < fine kaolinite. In an attempt to relate coking activity to substrate properties, total surface area data are shown in Figure 4a plotted in the above order. With the exception of sand, it is apparent that coking activity does not follow the total surface area series of Figure 4a. However, the macro pore surface area shown in Figure 4b does appear to track coke formation with the exception of illite.

Figure 5a shows the sum of meso and macro pore volume (pores > 2 nm) for each substrate. With two exceptions, illite and course-grained kaolinite, this plots also tracks the order of relative coking activity from Figure 3. The course-grained kaolinite had a greater pore volume than did the fine-grained kaolinite but showed relatively less coking activity. The reason for this anomaly may be due to the substantial difference in surface area between these two samples (Figure 4). That is, even though the course-grained kaolinite had a larger pore volume, the substantially lower surface area perhaps countered the larger pore volume. In the case of illite, the relatively high coking rate cannot be explained by either surface area or pore volume. We cannot explain the relatively high coke formation rate for illite though we suspect there may be a significant difference in active surface site concentration (or perhaps the absence of a carbon coating) relative to the other substrates.

Finally, Figure 5b shows the changes in the combusted shale pore volume as a function of exposure time at 620^0 C. As might be expected, this value steadily declines with increasing exposure time suggesting that the rate of coke formation may be decreasing as well. Such a decline was not detected by curve fitting the QMS data though data scatter could easily have obscured a small effect. Longer exposure times planned for future experiments should help clarify this point.

Acknowledgments. The authors gratefully acknowledge the work of D. Smith and J. Fannin for assisting with the experiments and data reduction, and M. Stewart, G. Thomas and M. Moore for analytical support. This work was supported in part by the Morgantown Energy Tech. Ctr., USDOE, under Coop. Agreement DE-FC21-90MC27286 (such support does not constitute an endorsement by the USDOE of the views expressed in this manuscript).

References

1. Taulbee, D.N. and Carter, S.D., *Fuel*, **70**, 1991, p. 1245-51.
2. Carter, S.D., Robl, T.L., Rubel, A.M., and Taulbee, D.N., *Fuel*, 1990, **69**, p 1124.
3. Levy, J.H., Mallon, R.G., and Wall, G.C., *Proc. 3rd Australian Workshop on Oil Shale*, Lucas Heights, NSW, 1986, p. 133.
4. Coburn, T.T., Taylor, R.W., Morris, C.J., and Duval, C., *Proc.: Int. Conf. on Oil Shale and Shale Oil*, Beijing, China, 1988, Colorado Sch. Mines Press.
5. Rubel, A.M., Rimmer, S.M., Keogh, R., Robl, T.L., Carter, S.D., and Derbyshire, F.J., *Fuel*, 1991, **70**, 1352.
6. Carter, S.D., Taulbee, D.N., Rubel, A.R., Abner, R.T., *Proc.: 1988 Eastern Oil Shale Symp.*,**IMMR88/101**, Inst. Min. & Minerals Res., Lexington, Ky., May., 1989, p. 333-340.
7. Carter, S.D., and Taulbee, D.N., submitted to *Fuel*, Jan. 1992.
8. Richardson, J.H., Huss, E.B., Ott, L.L., Clarkson, J.E., Bishop, M.O., Taylor, J.R., Gregory, L.J., and Morris, C.J., **Report UCID-19548**, 1982, LLNL, Livermore, Ca.
9. Wallman, P.H., Tamm, P.W., and Spars, B.G., *ACS Symp. Ser. 163*, 1981, p. 93.
10. Carter, S.D., *ACS Div. of Pet. Chem. Prep.*, 1987, **32**, #1, p. 133.

Table 1. Substrate properties. Substrates are 20X60 mesh unless otherwise noted.

Substrate	Origin	Preparation/comment
Pyrolyzed Shale	Cleveland oil shale	530C in N_2/10 min
Gasified Shale	Cleveland oil shale	800C in Steam/20 min
Combusted Shale	Cleveland oil shale	700C in air/10 min
Sand	Ottawa, Canada	20X30 mesh
Illite	Carbon deficient Huron Shale (Three Lick Member), Rowan Co, KY	
Kaolinite-F	Fine grained, Georgia, USA	
Kaolinite-C	Course grained, Georgia, USA	

Acid/base treated substrates were placed in an excess of .005 N NaOH or HCl overnight, exhaustively rinsed with distilled H_2O, and dried prior to exposure.

Table 2. Reactor Conditions.

PYROLYZER:

Shale Feedrate	12 g/min
Superficial gas velocity	0.46 m/s
Temperature	530°C
Bed Height	7.6 cm

SUBSTRATE BED:

Substrate load	100 g (~3 cm depth)
Temperature	530-660°C
Solid Residence Time	5, 10, 15 min

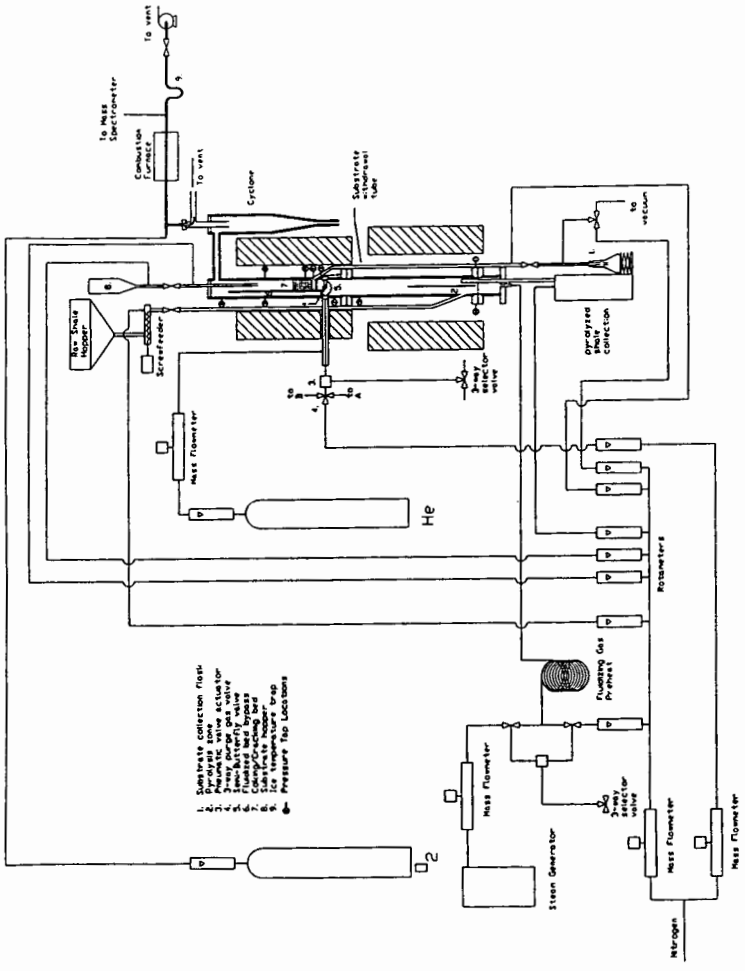
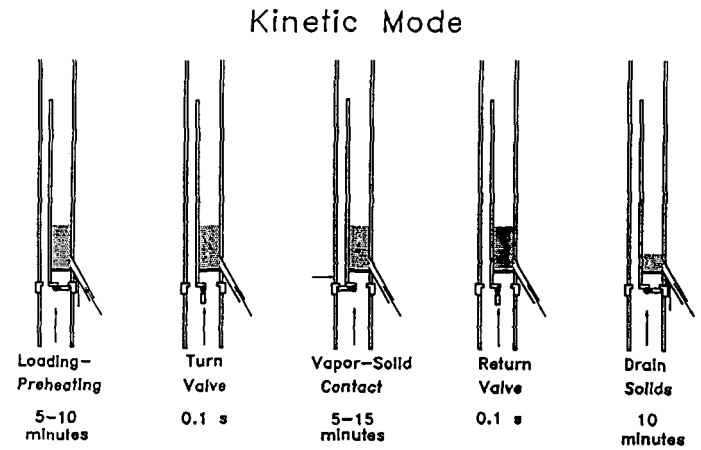


Figure 1. Flow diagram of the valved fluidized bed system for investigating the coking kinetics of shale oil vapors over solid materials.

Figure 2. Schematic of reactor configuration during coking sequence-Top. CO_2/Ar ratio (44/40 m/e) during typical coking sequence-Bottom.



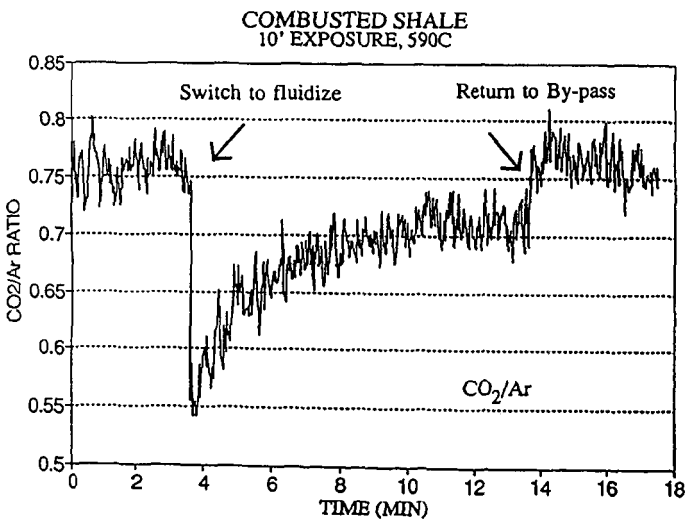
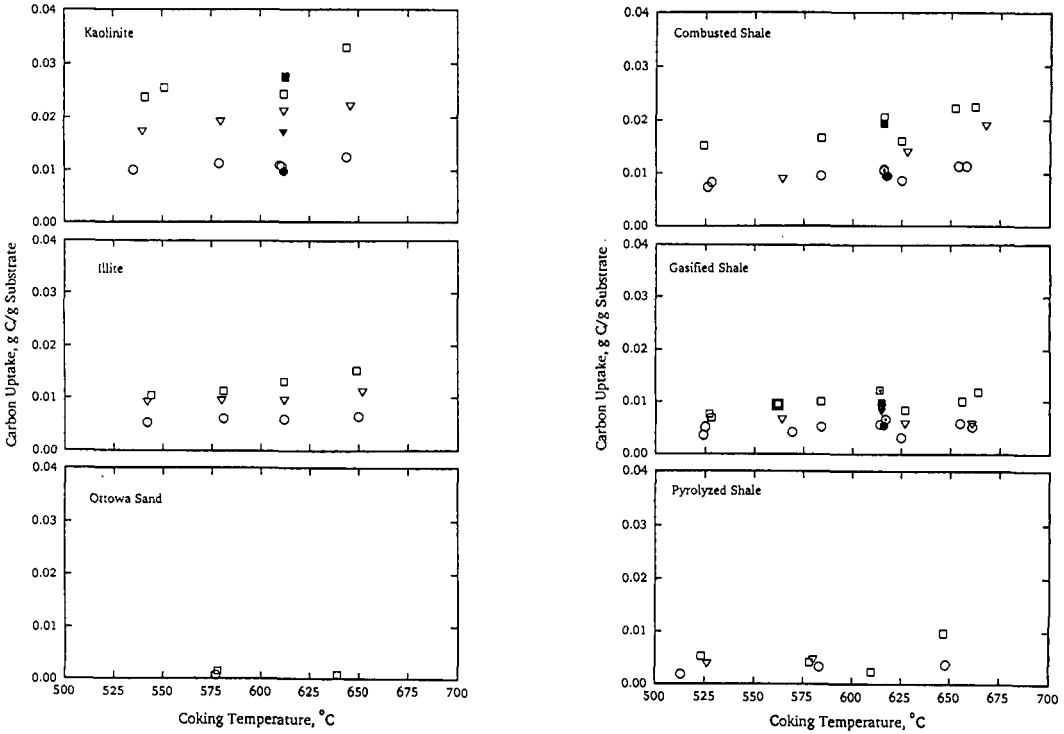


Figure 3. Average coke deposition as a function of exposure time and substrate temperature. ○-5 min, ▽-10 min, □-15 min. Filled symbols represent either course-grained kaolinite (kaolinite plot) or base treated combusted or gasified substrate, symbols with · represent acid treatment.



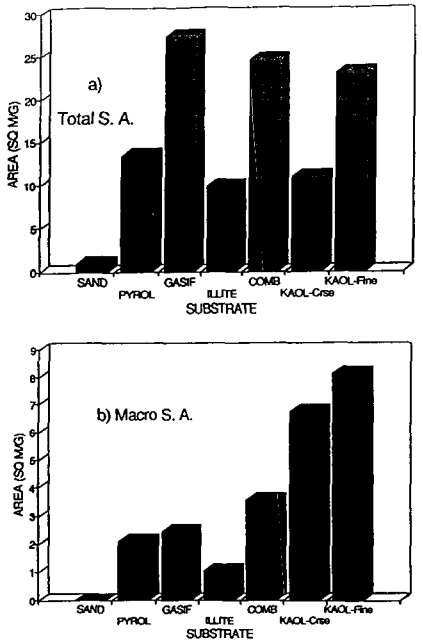


Figure 4. a) Total surface area b) Surface area within macro pores. Substrates shown in order of increasing coking activity.

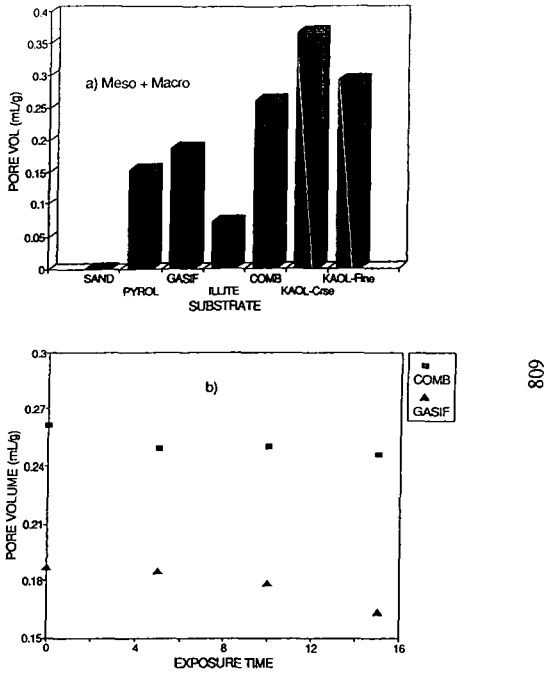


Figure 5. a) Meso + macro pore volume (mL/g substrate). b)-Changes in the meso + macro pore volume for combusted and gasified substrates as a function of exposure time at 620° C.